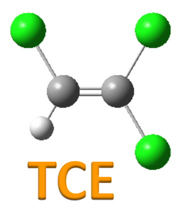
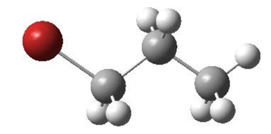
SERDP(WP-2522) Development of Azeotropic Blends to Replace TCE and nPB in Vapor Degreasing Operations

Darren L. Williams (PI); Jacob Perry; John Fecco; Robert Stanton; Nathan Thompson - Chemistry Department, Sam Houston State University, Huntsville, TX (936)294-1529 Williams@SHSU.edu with consultants: BFK Solutions LLC (Barbara and Ed Kanegsberg), Pacific Palisades, CA (310)459-3614 info@BFKSolutions.com

Program Objectives

Azeotropic blends that have similar solubility parameters and similar physical properties as trichloroethylene (TCE) and n-propyl bromide (nPB) but without undesirable environmental, occupational, safety, and health properties were tested as sustainable drop-in replacements for TCE and nPB in vapor degreasing operations,[1] also known generally as vapor phase cleaning.[2]





This work aimed to achieve the following specific objectives:

1. To develop azeotropic solvent blend alternatives to trichloroethylene (TCE) and n-propyl bromide (nPB) used in DoD vapor degreasing (VDG) operations.
2. To enable sustainable use of VDG equipment in the DoD by recommending alternatives that are not hazardous air pollutants (HAPs), volatile organic carbon (VOC) solvents, ozone depleting substances (ODS), or solvents with a high global warming potential (GWP).[3]
3. To produce a model-based approach to enable DoD users to continue to respond to future constraints on solvent-based cleaning operations.
4. To test the azeotropic alternatives head-to-head against TCE and nPB in VDG equipment with extensive characterization of the fluids and the cleaning effectiveness.

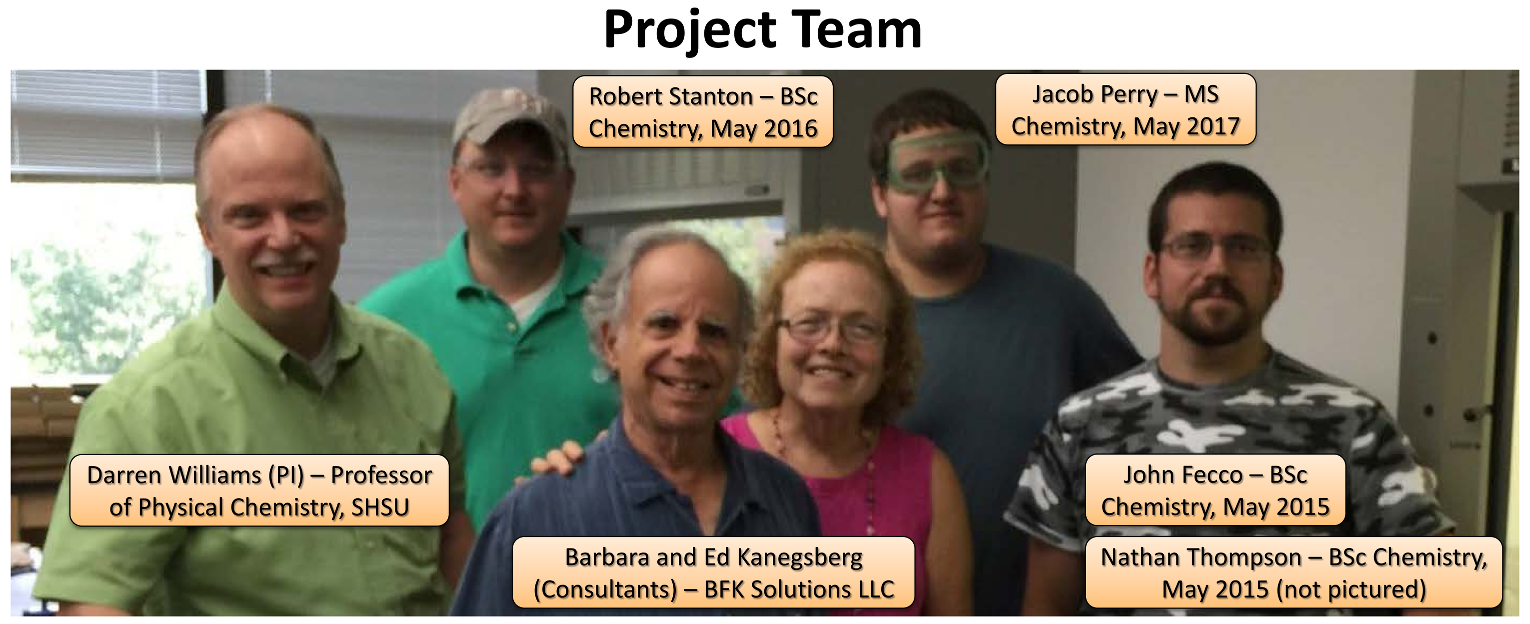
Background

Two solvents trichloroethylene (TCE) and n-propylbromide (nPB) are used in a wide variety of VDG applications, but the environmental, occupational, safety, and health (EOSH) profiles of these solvents are undesirable.[4] Some facilities are moving from these solvents to blends with trans-1,2-dichloroethylene (tDCE), but this is seen as an interim solution since tDCE is regulated as a VOC. Therefore, other azeotropic blends are needed as specified in the statement of need (SON).[1]

This project executed the following tasks to address the statement of need.

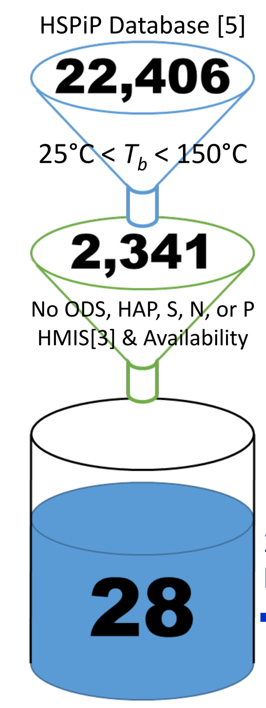
1. Collect literature values on HAPs, ODSs, VOCs, HSPs, PELs, HMIS, and Availability
2. Predict blend options and desirability
3. Screen the blends for azeotropic behavior using fractional distillation and Raman spectroscopy
4. Perform flash point screening tests using the Tag Closed Cup Method (ASTM D56)
5. Test degreasing ability using vial-based solvent transfer gravimetric measurements
6. Test defluxing ability using vial-based solvent transfer conductivity measurements
7. Create gallon scale quantities of promising azeotropic blends
8. Test azeotrope blends in comparison to TCE and nPB in vapor degreasing equipment
9. Characterize the physical properties (density, viscosity, and surface tension) of new azeotropes

Project Team



We sought input from over 250 contacts in 109 companies and agencies

Procedures, Materials, and Methods



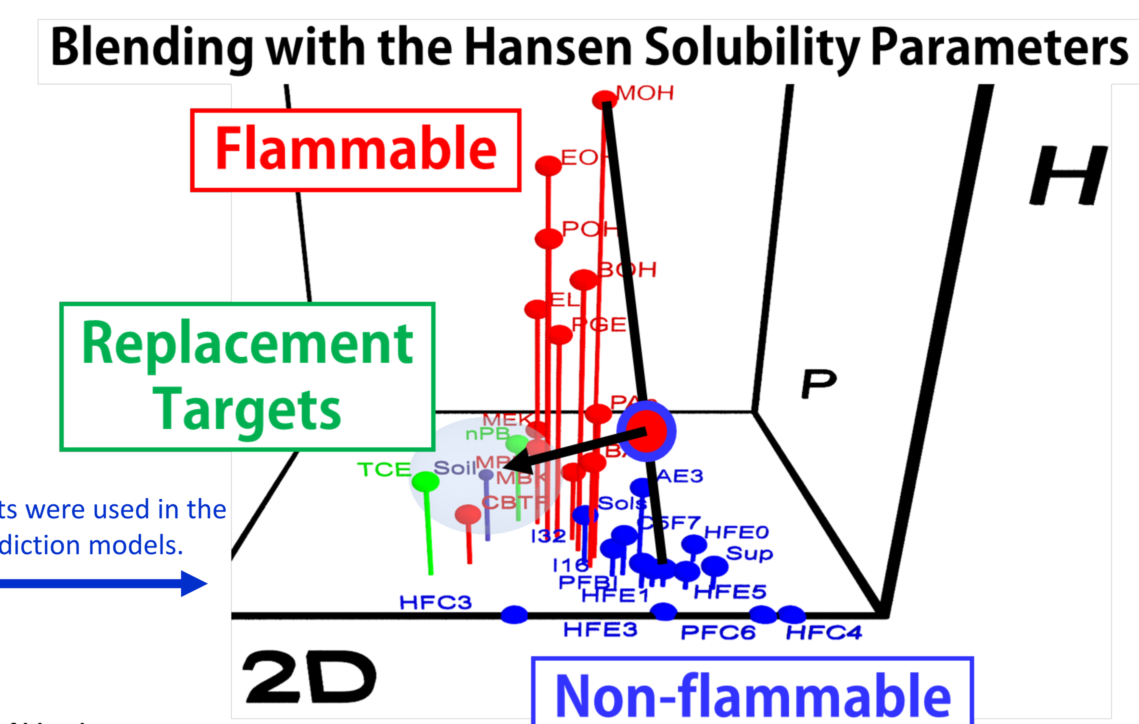
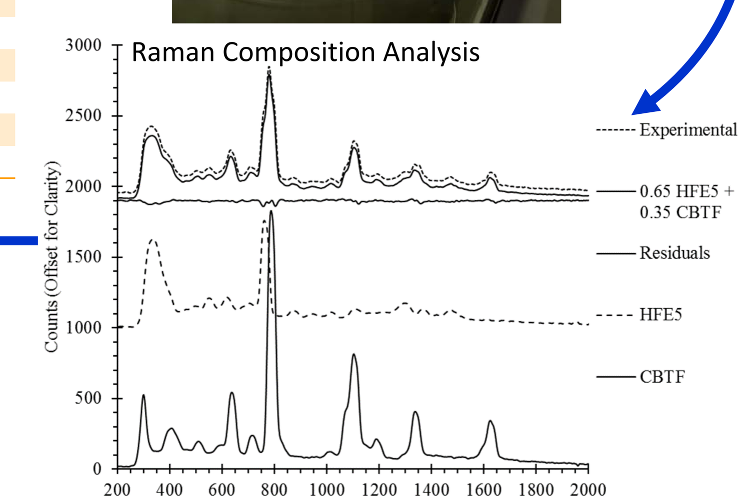


Table 1: The down-selected list of blend components.

CAS	Abbr	Name
106-94-5	nPB	1-bromopropane (n-propylbromide)
79-01-6	TCE	trichloroethylene
406-78-0	AE3	tetrafluoroethyltrifluoroethylether (AE3000)
15290-77-4	C5F7	heptafluorocyclopentane
405-58-6	HFC3	pentafluorobutane (HFC365)
138495-42-8	HFC4	decafluoropentane (HFC-4310mee)
375-03-1	HFE0	methoxyperfluoropropane (HFE-7000)
163702-07-6	HFE1	methoxyperfluorobutane (HFE-7100)
-	HFE3	methoxyperfluorohexane (HFE-7300)
297730-93-9	HFE5	ethoxyperfluoromethylhexane (HFE-7500)
355-43-1	I16	iodoperfluorohexane (I-1600)
677-69-0	I32	iodoheptafluoropropane (I-3200)
375-51-9	PFBI	iodononafluorobutane (2-PFBI)
355-42-0	PFC6	perfluorohexane (PFC 5060)
102687-65-0	Sols	trans-chlorotrifluoropropene (Solstice)
69296-04-4	Sup	methoxytridecafluoroheptene (Suprion)
540-88-5	BAC	tert-butylacetate
75-65-0	BOH	tert-butylalcohol
98-56-6	CBTF	para-chlorobenzotrifluoride
97-64-3	EL	ethyllactate
64-17-5	EOH	ethanol
108-10-1	MBK	methylisobutylketone (MIBK)
78-93-3	MEK	methylethylketone (MEK)
67-56-1	MOH	methanol
107-87-9	MPK	methylpropylketone
108-21-4	PAc	iso-propylacetate
107-98-2	PGE	propyleneglycolmonomethylether
67-63-0	POH	iso-propanol

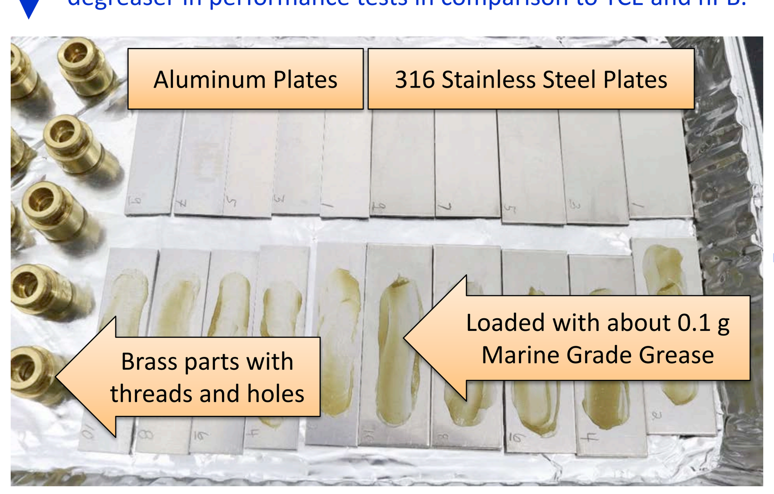
1:1 Mix

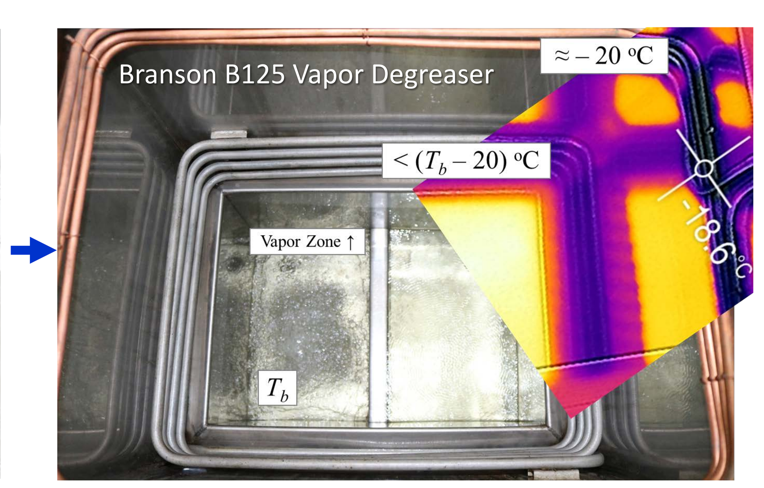
Distillates with low T_b characterized with Raman spectroscopy



Flashpoint test using ASTM D56, followed by vial-based grease and defluxing tests

Promising azeotropes were prepared for use in the vapor degreaser in performance tests in comparison to TCE and nPB.

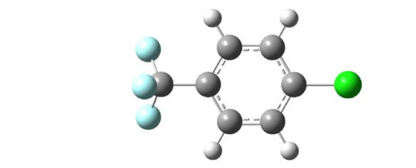


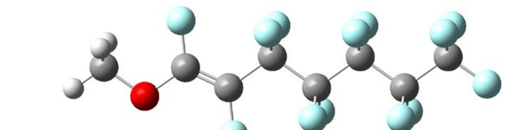


Results

Seven new azeotropic blends were discovered during this project.

- Four blends failed the flash point test.
- One failed the vial-based degreasing test.
- Two blends survived the flash point and degreasing tests.
  AZ6 (80% Suprion, 20% p-chlorobenzotrifluoride, T_b = 110 °C)
  AZ7 (65% HFE-7500, 35% p-chlorobenzotrifluoride, T_b = 125 °C)





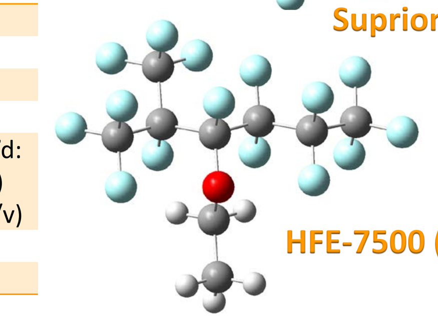
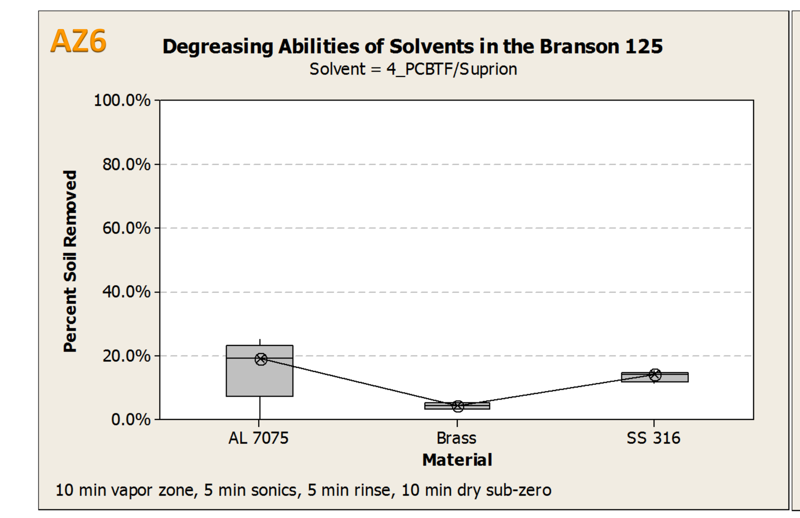


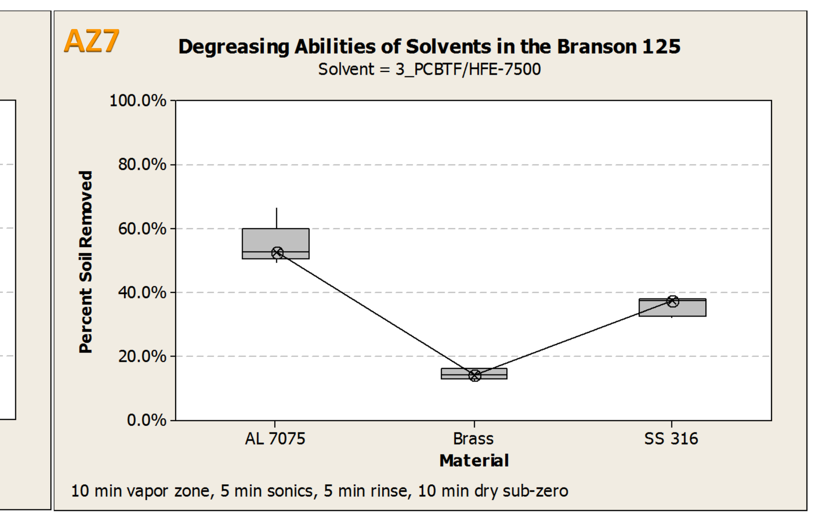
Table 2: Seven azeotropic blends discovered during this project

Abbr	Solvents #1	#2	T_b /°C	T_{flash} /°C	Comments
AZ1	85% HFE1	15% MOH		45.5	Failed Flashpoint
AZ2	85% AE3	15% MOH		48	Failed Flashpoint
AZ3	53% HFE3	47% tBAc	84	≤ 21	Failed Flashpoint
AZ4	50% AE3	50% HFC3		None	Very poor solvency
AZ5	83% HFE5 5% in LF 96% in HF	17% EL 95% in LF 4% in HF	112	≤ 50	Failed Flashpoint; 2 phase liq'd: Light fraction (LF) is 14% (v/v) Heavy fraction (HF) is 86% (v/v)
AZ6	80% Sup	20% CBTF	110	None	Carried forward to testing
AZ7	65% HFE5	35% CBTF	125	None	Carried forward to testing

Degreasing Tests

- AZ6 and AZ7 were evaluated in the vapor degreaser in comparison to the performance of nPB and TCE.
- All were required to clean marine-grade grease from SS316, Al7075, and brass parts with a 10-min vapor step, a 5-min 40-kHz ultrasonic step, a 5-min vapor rinse, and a 10-minute sub-zero drying step.
  - nPB and TCE removed 100% of the soil on all three part types as measured gravimetrically
  - AZ6 removed less than 20% of the soil (16(±11)% on Al7075, 13(±2)% on SS316, and 4(±1)% on brass)
  - AZ7 removed less than 60% of the soil (55(±7)% on Al7075, 36(±3)% on SS316, and 15(±2)% on brass)





Defluxing Test

A vial-based Resistivity of Solvent Extract (ROSE) test was developed for this project. Vials of melted solder paste were cleaned with solvent to measure the ionic contamination transferred and left behind by each solvent. The figure of merit was the percent of ionic contamination (P_{ion}) transferred by the solvent:

$$P_{ion} = \frac{C_t}{C_t + C_o}$$

where C_t is the blank-corrected conductivity of the transfer vials and C_o is the blank-corrected conductivity of the flux residue that remained in the original vial. AZ6 and AZ7 removed less than 20% of the removable ionic contamination.

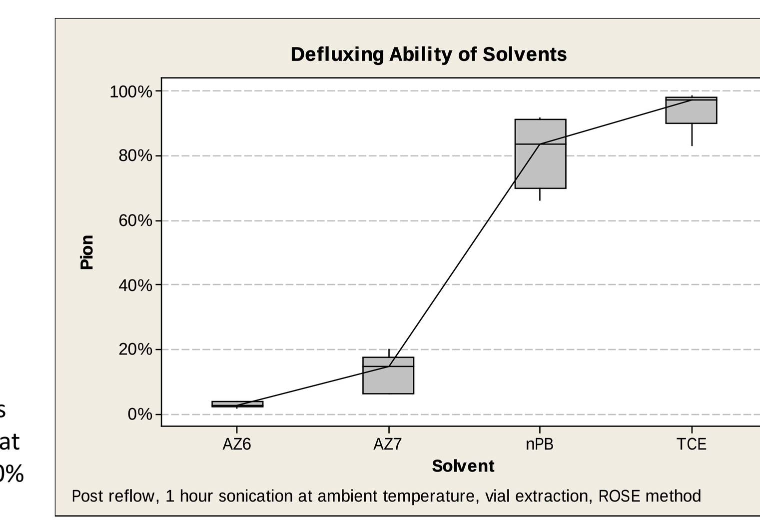


Table 3: The physical properties of the blend components, target solvents, and new azeotropic blends AZ6 and AZ7

Abbr	D $MPa^{1/2}$	P $MPa^{1/2}$	H $MPa^{1/2}$	ρ g/mL	β °C^{-1}	η cP	γ mN/m	W
HFE5	**13.3**	**2.0**	**1.0**	1.62(2)	1.55(2)×10^{-3}	1.08(3)	**16.2**	92.6(2)
Sup	**12.8**	**2.0**	**1.3**	1.57(6)	1.4(1.1)×10^{-3}	1.06(18)	**18**	82.2(8)
CBTF	**17.3**	**4.0**	**2.9**	1.333(3)	1.03(4)×10^{-3}	0.84(7)	**25**	63.6(1)
AZ6	13.7	2.4	1.6	1.521(2)	1.47(2)×10^{-3}	0.97(4)	18.8(1)	83.9(1)
AZ7	14.7	2.7	1.7	1.516(6)	1.58(5)×10^{-3}	0.94(5)	19.3(2)	83.6(1)
nPB	**16.4**	**7.9**	**4.8**	**1.3**		**0.49**	**25.9**	**105**
TCE	**18**	**3.1**	**5.3**	**1.5**		**0.53**	**28.7**	**99**

Bold text indicates literature values from suppliers and the HSPiP database.
Uncertainties for experimental data are in parentheses adjacent to the appropriate place value.

References

1. SERDP. FY 2015 STATEMENT OF NEED Weapons Systems and Platforms (WP) Program Area SUSTAINABLE SOLVENTS FOR USE IN DEGREASING. WPSEED-15-01. Strategic Environmental Research and Development Program (SERDP): Washington, DC 2013, pp 1–4.
2. Mouser, W. L. Organic Solvent Cleaning: Solvent and Vapor Phase Equipment Overview. In Handbook for Critical Cleaning - Cleaning Agents and Systems; Kanegsberg, B., Kanegsberg, E., Eds.; CRC Press Taylor & Francis: Boca Raton, FL, 2011; pp 363–372.
3. Hazard Communication, 29 CFR 1910, 1915, and 1926, OSHA, DOL. https://www.osha.gov/FedReg_osha_pdf/FED20120326.pdf ; USEPA (HAPs https://www.epa.gov/haps; ODS https://www.epa.gov/ozone-layer-protection/ozone-depleting-substances; VOCs https://www.epa.gov/indoor-air-quality-iaq/technical-overview-volatile-organic-compounds)
4. Chemical & Material Risk Management Program, Office of the Under Secretary of Defense for Acquisition, Technology, and Logistics, *C&M Emerging Risk Alert – 1-Bromopropane (1-BP or nPB)*. "ACGIH proposes TLV-TWA drop from 10ppm to 0.1ppm"
5. Abbott, S.; Hansen, C. M.; Yamamoto, H. *Hansen Solubility Parameters in Practice Complete with eBook* , Software and Data; 2013.

Acknowledgments

This work was funded by the Strategic Environmental Research and Development Program (SERDP) SEED Grant WP-2522.
Some student labor was funded by the Welch Foundation Departmental Development Grant X011.

Conclusions and Future Plans

1. Two new, high-boiling, non-flammable, low/no VOC azeotropic blends suitable for vapor degreasing were discovered.
2. The new blends contain **VOC-exempt CBTF** which has a low CEL of 25 ppm. However, CBTF also has a low vapor pressure (< 0.1 of nPB and < 0.05 of TCE) making the workplace exposure low and easily controlled.
3. The new blends are **not** suitable for replacing TCE or nPB in vapor degreasing operations.
4. The new blends **may** be decent at removing Krytox grease, based upon their Hansen solubility parameters.
5. A **new vial-based ROSE test** for defluxing trials was developed. *This will be submitted for publication in the Surface Mount Technology Association's (SMTA) Knowledgebase as a research article.*
6. **Ten new SOPs** were produced that are suitable for use by other DoD facilities. These are included in the Final Report of this project. The SOPs are 1. Gravimetric Analysis, 2. Liquid Density and Surface Tension Measurement, 3. Ball Drop Viscosity Measurement, 4. Fractional Distillation, 5. Raman Spectroscopic and Chemometric Analysis, 6. Closed Cup Flash Point Determination, 7. Solvent Comparison for Cleaning Grease, 8. Vapor Degreasing (Graduate Cylinder Method), 9. Vapor Degreasing (Branson B125), 10. Solvent Comparisons for Ionics Extraction from Solder Paste.
7. There is some interest in silicone-based solvents (OS-10, OS-20, and OS-30), so these will be studied in the future.